Derivation of quantum work equalities using quantum Feynman-Kac formula

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On the basis of a quantum mechanical analogue of the famous Feynman-Kac formula and the Kolmogorov picture, we present a novel method to derive nonequilibrium work equalities for isolated quantum systems, which include the Jarzynski equality and Bochkov-Kuzovlev equality. Compared with previous methods in the literature, our method shows higher similarity in form to that deriving the classical fluctuation relations, which would give important insight when exploring new quantum fluctuation relations.

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Feynman-Kac (FK) formula originally found by Feynman in quantum mechanics [1] and extended by Kac [2] establishes an important connection between partial differential equations and classical stochastic processes. Briefly, assuming that in a continuous diffusion process the probability of a stochastic trajectory X started from a state x' at time t' is $P[X|x',t']$. The solution $u(x',t')$ of the following partial differential equation

$$\begin{cases} \partial_{t'} u(x',t') = -\mathcal{L}^{+}(x',t')u(x',t') - g(x',t')u(x',t'), \\ u(x',t'=t) = q(x') \end{cases} \tag{1}$$

has a concise path integral representation [3]:

$$u(x',t') = \int \mathcal{D}X e^{\int_{t'}^{t} g(x_\tau,\tau)d\tau} q(x_t,t)P[X|x',t'], \tag{2}$$

where $\mathcal{L}^{+}$ is the Markovian generator of the diffusion. This is the famous FK formula in classical stochastic processes.

Pioneered by Lebowitz and Sphon [4], this formula was also found very useful in studying fluctuation relations [5–9]. In the past two decades, these important relations have greatly deepened our understanding about the second law of thermodynamics and nonequilibrium physics of small systems [4, 10–20]. Recently, finding quantum fluctuation relations is attracting intensive interests. Fruitful theoretical and experimental results [21–30] have been obtained. To our best knowledge, however, there is no work explicitly using the FK formula. At first glance, the reason is very obvious, because the classical trajectory picture on which the FK is based is not available in quantum physics. Contrary to the intuition, in this Rapid Communication we use an isolated quantum system as an example to show that there indeed exists a quantum mechanical analogue of the classical FK formula and it is very useful to derive the quantum nonequilibrium work relations including the Jarzynski [21, 23, 24] and Bochkov-Kuzovlev equalities [29].

Kolmogorov picture and backward invariable. We start by introducing essential notations and a new picture that is a quantum-mechanical analogue of Kolmogorov's idea [31] in classical stochastic theory. Although the picture is virtually equivalent to other well-known pictures, e.g. the Heisenberg picture, we will see later that it is very relevant with the time reversal concept. We assume that the closed quantum system is described by a time-dependent Hamiltonian $H(t)$. The system's density operators ρ at two different times t and t' ($< t$) are connected by the time-evolution operator $U(t')$, i.e.,

$$\rho(t) = U(t)U^{\dagger}(t')\rho(t')U(t')U^{\dagger}(t). \tag{3}$$

Given an arbitrary observable F that does not depend explicitly on time, we define its Kolmogorov picture as

$$F(t,t') = U(t')F^{\mathrm{H}}(t)U^{\dagger}(t'), \tag{4}$$

where the superscript H denotes the Heisenberg picture: $F^{\mathrm{H}}(t)=U^{\dagger}(t)FU(t)$. On the basis of Eqs. (3) and (4), the expectation value $\langle F\rangle(t)$ at time t in the picture is

$$\mathrm{Tr}[F\rho(t)] = \mathrm{Tr}[F(t,t')\rho(t')], \tag{5}$$

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and the equation of motion for $F(t,t')$ with respect to t' is simply

$$\begin{cases} i\hbar\partial_{t'}F(t,t') = -[F(t,t'),H(t')], \\ F(t,t'=t) = F. \end{cases} \tag{6}$$

We see that it is a terminal condition rather than initial condition problem. It is worth pointing out that Eq. (6) is very distinct from the motion equation of the same $F(t,t')$ with respect to the forward time t if the Hamiltonian explicitly depends on time.

Equation (5) has a trivial property: the time derivatives on both sides with respect to t' vanishes, or equivalently, $\mathrm{Tr}[F(t,t')\rho(t')]$ being a backward time invariable. The property is very analogous to that of the Chapman-Kolmogorov equation in the classical diffusion theory [32]. According to our previous experience which constructing a more general backward time invariable may lead into the classical fluctuation relations [9], it would be very interesting to explore whether the same idea is still true here. Imitating Eq. (5) in Ref. [8], we find there is very analogous backward time invariable in the quantum case:

$$\mathrm{Tr}[F\overline{\rho}(t)] = \mathrm{Tr}[\overline{F}(t,t')\overline{\rho}(t')], \tag{7}$$

if the new operator $\overline{F}(t,t')$ satisfies

$$\begin{aligned} i\hbar\partial_{t'}\overline{F}(t,t') = &-[\overline{F}(t,t'),H(t')] - \overline{F}(t,t')(i\hbar\partial_{t'}\overline{\rho}(t') + [\overline{\rho}(t'),H(t')])\overline{\rho}^{-1}(t') \\ &+([\overline{F}(t,t'),A(t')]B(t') + \overline{F}(t,t')[B(t'),A(t')])\overline{\rho}^{-1}(t') \end{aligned} \tag{8}$$

and its terminal condition at t is assumed to be F, where the operators $A(t')$, $B(t')$ and invertible density operator $\overline{\rho}(t')$ are arbitrary. The proof of Eq. (7) is straightforward. The meaning of the last two terms on the right hand side will appear when we chooses $\overline{\rho}(t')$ to be the system's density operator $\rho(t')$, i.e. the term $i\hbar\partial_{t'}\overline{\rho} + [\overline{\rho}, H]$ vanishing. The general Eq. (8) seem uncommon in the quantum mechanics except a specific case:

$$\begin{cases} i\hbar\partial_{t'}\overline{F}(t,t') = -[\overline{F}(t,t'),H(t')] - \overline{F}(t,t')O(t'), \\ \overline{F}(t,t'=t) = F, \end{cases} \tag{9}$$

where $O(t')$ is an arbitrary operator. We may easily write down its solution given by

$$\begin{aligned} \overline{F}(t,t') &= U(t')F^{\mathrm{H}}(t)\mathcal{T}_{+}e^{(i\hbar)^{-1}\int_{t'}^{t}d\tau U^{\dagger}(\tau)O(\tau)U(\tau)}U^{\dagger}(t') && (10)\\ &= U(t')F^{\mathrm{H}}(t)Q(t,t')U^{\dagger}(t'), && (11) \end{aligned}$$

where $\mathcal{T}_{+}$ is the time-ordering operator. We simply name Eq. (10) quantum FK formula because of its highly formal similarity to the classical FK formula (2). However, we must remind the reader that the whole time-ordering term, which we specially denote it by a operator $Q(t,t')$ for convenience, only indicates that the operator satisfies

$$i\hbar\partial_{t'}Q(t,t') = -Q(t,t')[U^{\dagger}(t')O(t')U(t')] \tag{12}$$

with a terminal condition $Q(t,t'{=}t){=}1$. So far, we mainly concentrate on a formal development; the physical relevance of the quantum FK formula (10) and the backward time invariable (7) is not obvious. In the following we show that these results would lead into the quantum Jarzynski and Bochkov-Kuzovlev equalities if one chose specific $\overline{\rho}(t')$, $A(t')$, and $B(t')$.

Quantum Jarzynski equality. We assume that the closed quantum system is initially in thermal equilibrium with a density operator $\rho_{\mathrm{eq}}(0){=}e^{-\beta H(0)}/Z(0)$, where the partition function $Z(0){=}\mathrm{Tr}[e^{-\beta H(0)}]{=}e^{-\beta G(0)}$, β is inverse temperature and $G(0)$ is the initial free energy. At later times the system evolutes under the time-dependent Hamiltonian $H(t)$. We choose $A{=}B{=}0$, $\overline{\rho}(t')$ to be the instant equilibrium state $\rho_{\mathrm{eq}}(t'){=}e^{-\beta H(t')}/Z(t')$ with the instant partition function $Z(t'){=}\mathrm{Tr}[e^{-\beta H(t')}]{=}e^{-\beta G(t')}$. Equation (8) then becomes

$$i\hbar\partial_{t'}\overline{F}(t,t') = -[\overline{F}(t,t'),H(t')] - i\hbar\overline{F}(t,t')\partial_{t'}\rho_{\mathrm{eq}}(t'){\rho_{\mathrm{eq}}}^{-1}(t'). \tag{13}$$

Obviously, the above equation follows the structure of Eq. (9) and especially

$$O(t') = i\hbar[\partial_{t'}e^{-\beta H(t')}e^{\beta H(t')} + \beta\partial_{t'}G(t')] \tag{14}$$

when we substitute the expression of $\rho_{\mathrm{eq}}(t')$ into the "source" term of Eq. (13). Intriguingly, in this case Eq. (12) indeed has a very simple analytical solution

$$Q(t,t') = [U^{\dagger}(t)e^{-\beta H(t)}U(t)]U^{\dagger}(t')e^{\beta H(t')}U(t')]e^{\beta[G(t)-G(t')]}. \tag{15}$$

Hence, on the basis of Eqs. (7), (10), and (15) we obtain

$$\begin{aligned} \mathrm{Tr}[F\rho_{\mathrm{eq}}(t)] &= \mathrm{Tr}[U(t')F^{\mathrm{H}}(t)\mathcal{T}_{+}e^{\int_{t'}^{t}d\tau U^{\dagger}(\tau)\partial_{\tau}\rho_{\mathrm{eq}}(\tau)\rho_{\mathrm{eq}}^{-1}(\tau)U(\tau)}U^{\dagger}(t')\rho_{\mathrm{eq}}(t')] &(16)\\ &= \mathrm{Tr}[F^{\mathrm{H}}(t)e^{-\beta H^{\mathrm{H}}(t)}e^{\beta H^{\mathrm{H}}(t')}U^{\dagger}(t')\rho_{\mathrm{eq}}(t')U(t')]\ e^{\beta[G(t)-G(t')]}. &(17)\end{aligned}$$

If F=1 and t'=0 Eq. (17) is just the quantum Jarzynski equality on the inclusive work [24]:

$$\langle e^{-\beta H^{\mathrm{H}}(t)}e^{\beta H(0)}\rangle_{\mathrm{eq}}(0) = e^{-\beta\Delta G(t)}, \tag{18}$$

where $\Delta G(t)$=$G(t)-G(0)$, and we have used $\langle\ \rangle_{\mathrm{eq}}(0)$ to denote an average over the initial density operator $\rho_{\mathrm{eq}}(0)$. Additionally, Eq. (17) at t'=0 is also a specific case of the general functional relation given by Andrieux and Gaspard earlier; see Eq. (12) therein [26].

Bochkov-Kuzovlev equality. Here we consider a special realization of the time-dependent Hamiltonian [33]: a dynamic perturbation $H_1(t)$ $(t\geq 0)$ is applied on a system that is initially in thermal equilibrium with a time-independent H_{o}, that is, the total Hamiltonian at later times is $H_{\mathrm{p}}(t)$=H_{o}+$H_1(t)$. We have used the subscripts o and p to indicate "perturbed" and "original", respectively. Obviously, the system's initial density operator is $\rho_{\mathrm{p}}(0)$=ρ_{o}=$e^{-\beta H_{\mathrm{o}}}/Z_{\mathrm{o}}$, where the partition function Z_{o}=$\mathrm{Tr}[e^{-\beta H_{\mathrm{o}}}]$=$e^{-\beta G_{\mathrm{o}}}$. Choosing $H(t')$=H_{o}, $A(t')$=$-H_1(t')$, $B(t')$=$\overline{\rho}(t')$=ρ_{o} in Eq. (8), we obtain the following equation

$$\begin{aligned} i\hbar\partial_{t'}\widetilde{F}(t,t') &= -[\widetilde{F}(t,t'),H_{\mathrm{o}}]-([\widetilde{F}(t,t'),H_1(t')]-\widetilde{F}(t,t')[\rho_{\mathrm{o}},H_1(t')]\rho_{\mathrm{o}}^{-1}\\ &= -[\widetilde{F}(t,t'),H_{\mathrm{p}}(t')]-\widetilde{F}(t,t')[\rho_{\mathrm{o}},H_1(t')]\rho_{\mathrm{o}}^{-1}. &(19)\end{aligned}$$

We have used a new symbol $\widetilde{F}$ to distinguish it from the previous $\overline{F}$ because they satisfy different equations. We see that the above equation also follows the structure of Eq. (9), and especially

$$O(t') = [e^{-\beta H_{\mathrm{o}}},H_1(t')]e^{\beta H_{\mathrm{o}}}. \tag{20}$$

It would be interesting to check whether there is a simple analytical solution to Eq. (12) under this circumstance. We find that it indeed has:

$$Q(t,t') = [U_{\mathrm{p}}^{\dagger}(t)e^{-\beta H_{\mathrm{o}}}U_{\mathrm{p}}(t)][U_{\mathrm{p}}^{\dagger}(t')e^{\beta H_{\mathrm{o}}}U_{\mathrm{p}}(t')]. \tag{21}$$

Using Eqs. (7), (10), and (21) we establish another equality given by

$$\begin{aligned} \mathrm{Tr}[F\rho_{\mathrm{o}}] &= \mathrm{Tr}[U_{\mathrm{p}}(t')(F)_{\mathrm{p}}^{\mathrm{H}}(t)\mathcal{T}_{+}e^{(i\hbar)^{-1}\int_{t'}^{t}d\tau U_{\mathrm{p}}^{\dagger}(\tau)[\rho_{\mathrm{o}},H_1(\tau)]\rho_{\mathrm{o}}^{-1}U_{\mathrm{p}}(\tau)}U_{\mathrm{p}}^{\dagger}(t')\rho_{\mathrm{o}}] &(22)\\ &= \mathrm{Tr}[(F)_{\mathrm{p}}^{\mathrm{H}}(t)e^{-\beta(H_{\mathrm{o}})_{\mathrm{p}}^{\mathrm{H}}(t)}e^{\beta(H_{\mathrm{o}})_{\mathrm{p}}^{\mathrm{H}}(t')}U_{\mathrm{p}}^{\dagger}(t')\rho_{\mathrm{o}}U_{\mathrm{p}}(t')]. &(23)\end{aligned}$$

where $(F)_{\mathrm{p}}^{\mathrm{H}}(t)$=$U_{\mathrm{p}}^{\dagger}(t)FU_{\mathrm{p}}(t)$. If F=1 and t'=0 Eq. (23) is the quantum Bochkov-Kuzovlev equality on the exclusive work

$$\langle e^{-\beta(H_{\mathrm{o}})_{\mathrm{p}}^{\mathrm{H}}(t)}e^{\beta H_{\mathrm{o}}}\rangle_{\mathrm{o}} = 1 \tag{24}$$

that was proposed very recently in Ref. [29], where $\langle\ \rangle_{\mathrm{o}}$ indicates an average over the initial density operator ρ_{o}.

On the other hand, a distinction between the original and perturbed systems is not absolute. In physics we may regard $H_{\mathrm{p}}(t)$ as the original quantum system while H_{o} is perturbed system if the dynamic perturbation of the latter is thought to be $-H_1(t)$. Exchanging the subscripts p and o and changing the sign before H_1 into minus in Eq. (19), we then obtain another equation given by

$$i\hbar\partial_{t'}\widehat{F}(t,t') = -[\widehat{F}(t,t'),H_{\mathrm{o}}(t')]+\widehat{F}(t,t')[\rho_{\mathrm{p}},H_1(t')]\rho_{\mathrm{p}}^{-1}. \tag{25}$$

Of course, the argument can be as well strictly proved by choosing $H(t')$=$H_{\mathrm{p}}(t')$, $A(t')$=$H_1(t')$, and $B(t')$=$\overline{\rho}(t')$=$\rho_{\mathrm{p}}(t')$ in Eq. (8). We are interested in what new equalities like Eqs. (22) and (23) will be yielded. Doing analogous derivations, we have the following results:

$$\begin{aligned} \mathrm{Tr}[F\rho_{\mathrm{p}}(t)] &= \mathrm{Tr}[U_{\mathrm{o}}(t')F^{\mathrm{I}}(t)\mathcal{T}_{+}e^{-(i\hbar)^{-1}\int_{t'}^{t}d\tau U_{\mathrm{o}}^{\dagger}(\tau)[\rho_{\mathrm{p}}(\tau),H_1(\tau)]\rho_{\mathrm{p}}^{-1}(\tau)U_{\mathrm{o}}(\tau)}U_{\mathrm{o}}^{\dagger}(t')\rho_{\mathrm{p}}(t')] &(26)\\ &= \mathrm{Tr}[F^{\mathrm{I}}(t)(\rho_{\mathrm{p}})^{\mathrm{I}}(t)(\rho_{\mathrm{p}}^{-1})^{\mathrm{I}}(t')U_{\mathrm{o}}^{\dagger}(t')\rho_{\mathrm{p}}(t')U_{\mathrm{o}}(t')], &(27)\end{aligned}$$

where $F^{\rm I}(t)$ and $\rho_{\rm p}^{\rm I}(t)$ are the interaction pictures of the observable and density operator, respectively, e.g. $F^{\rm I}(t){=}U_{\rm o}^\dagger(t)FU_{\rm o}(t)$. Particularly, if $F{=}1$ and $t'{=}0$, Eq. (27) becomes

$$\langle(\rho_{\rm p})^{\rm I}(t)e^{\beta H_{\rm o}}\rangle_{\rm o} = e^{\beta G_{\rm o}}. \tag{28}$$

So far, we are not very clear what physics the equality reveals, though its first order approximation should be related to the famous fluctuation-dissipation theorems [33].

Time reversal. In the remaining part we want to give time reversal explanations of Eqs. (13), (19), and (25), which is essential to understand the physical meaning of the backward time t' and the origin of these three equations. We use Eq. (13) as an illustration. Multiplying its both sides with $\rho_{\rm eq}(t')$ and introducing a parameter $s{=}t{-}t'$ $(0{<}s{<}t)$, we rearrange the equation into

$$i\hbar\partial_s[\overline{F}(t,t-s)\rho_{\rm eq}(t-s)] = [\overline{F}(t,t-s)\rho_{\rm eq}(t-s), H(t-s)]. \tag{29}$$

Noting this is an initial condition rather than the terminal condition problem. Equation (29) seems very analogous to an evolution equation of a density operator, which is indeed true if we multiply both sides of the equation by the antiunitary time-reversal operator Θ and its conjugation to obtain

$$i\hbar\partial_s\overline{\rho}_{\rm R}(s) = [\overline{H}_{\rm R}(s), \overline{\rho}_{\rm R}(s)], \tag{30}$$

where the time-reversed density operator and time-reversed Hamiltonian are

$$\overline{\rho}_{\rm R}(s) \;=\; \frac{1}{{\rm Tr}[F\rho_{\rm eq}(t)]}\Theta\overline{F}(t,t-s)\rho_{\rm eq}(t-s)\Theta^\dagger, \tag{31}$$

$$\overline{H}_{\rm R}(s) \;=\; \Theta H(t-s)\Theta^\dagger, \tag{32}$$

respectively, and the coefficient is for the normalization of $\overline{\rho}_{\rm R}(s)$. Equation (31) immediately explains the backward time invariable in the Jarzynski equality case. Additionally, one may also prove that the same equation is equivalent to the key Lemma in Ref. [26] that was used to prove the functional relation; see the Appendix. Doing very similar calculations, we find that Eq. (19) is equivalent to the evolution equation of the time-reversed density operator $\widetilde{\rho}_{\rm R}(s)$ with Hamiltonian $\widetilde{H}_{\rm R}(s)$, which are given by

$$\widetilde{\rho}_{\rm R}(s) \;=\; \frac{1}{{\rm Tr}[F\rho_{\rm o}]}\Theta\widetilde{F}(t,t-s)\rho_{\rm o}\Theta^\dagger, \tag{33}$$

$$\widetilde{H}_{\rm R}(s) \;=\; \Theta H_{\rm p}(t-s)\Theta^\dagger = H_{\rm o} + \Theta H_1(t-s)\Theta^\dagger, \tag{34}$$

respectively, and Eq. (25) is equivalent to another evolution equation, the time-reversed density operator and Hamiltonian of which are

$$\widehat{\rho}_{\rm R}(s) \;=\; \frac{1}{{\rm Tr}[F\rho_{\rm o}]}\Theta\widehat{F}(t,t-s)\rho_{\rm p}(t-s)\Theta^\dagger, \tag{35}$$

$$\widehat{H}_{\rm R}(s) \;=\; \Theta H_{\rm o}\Theta^\dagger = H_{\rm o}, \tag{36}$$

respectively. Comparing the above three time reversal explanations in the same dynamic perturbation problem, we see that, though the original and time-reversed Hamiltonian for the quantum Jarzynski equality is completely the same with that for the quantum Bochkov-Kuzovlev equality, the time-reversed density operators have very distinct initial conditions, i.e., $\overline{\rho}_{\rm R}(0){=}\rho_{\rm eq}(t)$ and $\widetilde{\rho}_{\rm R}(0){=}\rho_{\rm o}$. Intriguingly, for the equality (28), the time-reversed Hamiltonian is overlapped with the original one, both of which are the unperturbed $H_{\rm o}$, while the initial conditions of the time-reversed density operator and the original one are different: they are $\rho_{\rm p}(t)$ and $\rho_{\rm o}$, respectively.

Conclusions. In this work, we have used a quantum mechanical analogue of the classical FK formula to derive known quantum nonequilibrium work relations in isolated quantum systems. Compared with the previous methods in the literature, our method shows highly similar in form to that for the classical fluctuation relations which we developed earlier [9]. We think that it is insightful because one may find the backward time invariable first and then give its physical interpretation rather than vise versa. Previous work has shown that direct defining nonequilibrium physical quantities was very nontrivial in quantum case [28]. Extending our method into more complicated quantum systems, e.g. the open quantum systems would be a challenge in our following researches.

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I. APPENDIX

Equation (31) could be further simplified. the time reversed density operator at later time s is connected with the initial condition by

$$\overline{\rho}_{\mathrm{R}}(s)=U_{\mathrm{R}}(s)\overline{\rho}_{\mathrm{R}}(0)U_{\mathrm{R}}^{\dagger}(s)=\frac{1}{\mathrm{Tr}[F\rho_{\mathrm{eq}}(t)]}U_{\mathrm{R}}(s)\Theta F\rho_{\mathrm{eq}}(t)\Theta^{\dagger}U_{\mathrm{R}}^{\dagger}(s), \tag{37}$$

where $U_{\mathrm{R}}(s)$ is the time-evolution operator for the time-reversed Hamiltonian $\overline{H}_{\mathrm{R}}(s)$. Substituting the above equation and the solution of Eq. (13)

$$\overline{F}(t,t')=U(t')F^{\mathrm{H}}(t)e^{-\beta H^{\mathrm{H}}(t)}e^{\beta H^{\mathrm{H}}(t')}U^{\dagger}(t')e^{\beta[G(t)-G(t')]} \tag{38}$$

into Eq. (31) and doing a simple calculation we obtain

$$U_{\mathrm{R}}(s)=\Theta U(t-s)U^{\dagger}(t)\Theta^{\dagger}. \tag{39}$$

[1] R. P. Feynman, Rev. Mod. Phys. **20** 367 (1948).
[2] M. Kac, Trans. Amer. Math. Soc. **65** 1 (1949).
[3] D. W. Stroock and S. R. S. Varadhan, *Multidimensinal Diffusion Processes*, (Springer, New York, 1979).
[4] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
[5] G. Hummer and A. Szabo, Proc. Proc. Natl. Acad. Sci. USA **98**, 3658 (2001).
[6] R. Chetrite and K. Gawedzki, Commun. Math. Phys. **282**, 469 (2008).
[7] H. Ge and D. Q. Jiang, J. Stat. Phys. **131**, 675 (2008).
[8] F. Liu and Z. C. Ou-Yang, Phys. Rev. E **79** 060107(R) (2009).
[9] F. Liu, H. Tong, R. Ma and Z. C. Ou-Yang J. Phys. A: *Math. Theor.* **43** 495003 (2010).
[10] G. N. Bochkov and Yu E. Kuzovlev, Sov. Phys. JETP **45** 125 (1977).
[11] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[12] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[13] J. Kurchan, J. Phys. A, **31**, 3719 (1998).
[14] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997); Phys. Rev. E. **56**, 5018 (1997).
[15] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999); Phys. Rev. E **61**, 2361 (2000).
[16] T. Hatano and S. I. Sasa, Phys. Rev. Lett. **86**, 3463 (2001).
[17] C. Maes, Sem. Poincare, **2**, 29 (2003).
[18] U. Seifert, Phy. Rev. Lett. **95**, 040602 (2005).
[19] T. Speck and U. Seifert, J. Phys. A **38**, L581 (2005).
[20] C. Bustamante, J. Liphardt, and F. Ritort, Phys. Today **58**(7) 43 (2005).
[21] J. Kurchan, arXiv: cond-mat/0007360 (2000).
[22] S. Yukawa, J. Phys. Soc. Jpn. **69**, 2367 (2000).
[23] H. Tasaki, arXiv:cond-mat/0009244 (2000).
[24] P. Talkner, E. Lutz, and P. Hänggi, Phys. Rev. E **75**, 050102 (2007).
[25] P. Talkner and P. Hänggi, J. Phys. A **40**, F569 (2007).
[26] D. Andrieux and P. Gaspard, Phys. Rev. Lett. **100**, 230404 (2008).
[27] M. Esposito, U. Harbola and S. Mukamel, Rev. Mod. Phys. **81**, 1665 (2009).
[28] M. Campisi, P. Hänggi, and P. Talkner, Rev. Mod. Phys. **83**, 771 (2011).
[29] Campisi M, Talkner P and Hänggi, Phil. Trans. R. Soc. A **369**, 291 (2011).
[30] S. Nakamura, et al. Phys. Rev. Lett. **104**, 080602 (2010).
[31] A. Kolmogorov, Mathematische Annalen **104**, 415 (1931).
[32] C.W. Gardiner 1983 *Handbook of stochastic methods* (Berlin: Springer).
[33] R. Kubo, J. Phys. Soc. Jpn. **12** 570 (1957).